Nitrate and Pesticide Residue Penetration into Aquifers - The Springfield Corners Profile

G.J. Kraft, B.A. Browne, W. DeVita, and D.J. Mechenich

College of Natural Resources

University of Wisconsin - Stevens Point

June 30, 2004

Nitrate and Pesticide Residue Penetration into Aquifers - The Springfield Corners Profile

G.J. Kraft, B.A. Browne, W. DeVita, and D.J. Mechenich

July 14, 2004

ABSTRACT

The leakage of NO_3 and pesticide residues from agricultural landscapes to groundwater has important implications for drinking water and aquatic ecosystems. This leakage increased greatly due to the large increase in fertilizer-N and pesticide use that began about 1960 and levelled in the 1980-1990s. Good progress has been made at describing the current geographical distribution of NO_3 and pesticide residues in groundwater, but the picture is murky as to what future conditions will emerge. Given that the increase in pollutant leakage is recent compared with typical groundwater residence times, modern aquifer pollutant loads (i.e., pollutant mass in aquifer storage) are unlikely in general to be in equilibrium with modern pollutant leakage. Equilibrium requires that either (1) degradation mechanisms eliminate pollutants at the rate at which they are loaded, or (2) groundwater with a modern pollutant load penetrates an entire aquifer thickness.

We examined NO_3 and pesticide penetration in a groundwater profile at the Springfield Corners site in northwest Dane County, Wisconsin. The area has a hummocky glacial topography, silt loam soils, and farming for dairy production and cash grain. Fields are usually planted to field corn, soybean, and hay crops. We focused on groundwater conditions in the 22 m thick saturated zone of the 44 m thick till, and in the 57 m thick "upper bedrock aquifer" (Tunnel City and Wonewoc sandstones). Till groundwater originates as recharge from within a few tens of meters of the Springfield Corners site, hence its quality is determined by very localized land uses. Upper bedrock aquifer groundwater originates over a broader area, up to 2-3 km from the study site, and hence is reflective of land covers over a representative portion of the landscape.

Groundwater samples were obtained at discrete depths in the profile and subjected to analyses for N species (including denitrification gasses), chlorofluorohydrocarbons for age-dating, pesticide residues (mainly those of atrazine and chloroacetanilides), and major ions. Till groundwater exhibited age dates of 1977 to 1986 and contained 13.6 to 19.1 mg L^{-1} of NO_3-N. Pesticide residue detections in the till were metolachlor ESA and alachlor ESA, at summed concentrations ranging up to 4 µg L^{-1}. Denitrification did not remove a substantial portion of NO_3 pollution.

Upper bedrock groundwater exhibited age dates of 1985 (aquifer top) to 1963 (aquifer base). Nitrate-N declined linearly with depth, from 13.2 mg L^{-1} to 0.9 mg L^{-1}. The upper 17 m of the profile exceeded the 10 mg L^{-1} NO_3-N drinking water and Wisconsin Enforcement standards. Nitrate concentrations increased linearly over time, and crossed a threshold in 1979 whereby incoming groundwater began to exceed the NO_3 MCL. Nitrate-N removal by denitrification was remarkably consistent, averaging 2.9 mg L^{-1}. Denitrification was relatively effective in removing NO_3-N when loads were small (up to 74% in early 1960s groundwater) but inefficient when loads increased (only 16% in 1980s groundwater). Detected pesticide residues were alachlor ESA, metolachlor ESA, and atrazine plus its deethyl, deisopropyl, and diamino degradates. Summed atrazine residues ranged from undetectable to 0.48 µg L^{-1}. Alachlor ESA detections were typically 1.0-1.5 µg L^{-1}. Metolachlor ESA concentrations were small (0.3-0.4 µg L^{-1}). Pesticide residue concentrations were greater in younger and shallower groundwater.

The upper bedrock aquifer is not fully penetrated by modern pollutant loads. Denitrification does not limit NO_3 penetration, and groundwater degradation mechanisms may not be limiting pesticide residue penetration. Hence, an equilibrium does not exist between modern pollutant loading and upper bedrock aquifer groundwater, and the aquifer's pollutant load will increase over time. Assuming that under modern practices NO_3-N will increase from the current 5.7 mg L^{-1} profile average to the 13.2 mg L^{-1} displayed in the most recent groundwater (1985), the aquifer average concentration would increase 230% at equilibrium. Because NO_3 trends show no sign of leveling, increases could be greater. Using similar assumptions, profile averaged summed pesticide residue concentrations would increase 330%. However, uncertainty about future pesticide use patterns and degradation rates make attempts to predict future pesticide conditions largely speculative.

The agricultural, hydrological, and geochemical conditions at the Springfield Corners site are similar to much of southcentral and southwest Wisconsin. We conclude tthat similar increases in groundwater pollutant loads in the Cambrian-Ordovician aquifer could result.

ACKNOWLEDGEMENTS

INTRODUCTION

The leakage of NO_3 and pesticide residues from agricultural landscapes to groundwater has important implications for drinking water quality and aquatic ecosystem health. This leakage increased greatly due to the large increases in fertilizer-N and pesticide use that began about 1960 and did not level until the 1980-90s (Figure 1). Though substantial progress has been made at describing current groundwater NO_3 and pesticide conditions (e.g., VandenBrook et al., 2002; Kolpin et al. 1993a; 1993b), a picture of the future remains cloudy. Given that the increase in pollutant leakage is recent compared with typical groundwater residence times, modern aquifer pollutant loads (i.e., pollutant mass in aquifer storage) are unlikely in general to be in equilibrium with modern pollutant leakage. "Equilibrium" is defined here as the condition in which the total mass of pollutant and its spatial distribution in an aquifer remain more-or-less constant over time. This condition can occur under one or both of the following: (1) degradation mechanisms eliminate pollutants at the rate at which they are loaded, or (2) groundwater with a modern pollutant load penetrates an entire aquifer thickness. Additional information on the NO_3 and pesticides in groundwater is summarized in Kraft et al. (2004).

The major goal of this study was to learn about the penetration of NO_3 and pesticide residues into Wisconsin's Cambrian-Ordovician aquifer (Figure 2), with a focus on the "upper bedrock aquifer" of Dane County at Springfield Corners. The objectives were to (1) determine the extent to which NO_3 and pesticide residues have penetrated the aquifer at the study site; and (2) ascertain whether these pollutants are accumulating or, alternatively, an equilibrium has been reached.

Previously we investigated NO_3 and pesticide residue penetration in the Stockton Study Area on the Wisconsin Central Sand Plain (Kraft et al., 2004), a setting much different than Springfield Corners. The Stockton Study Area has excessively drained sandy soils that poorly hold and cycle nutrients, pesticides, and water. These are underlain by ~30 m of coarse glaciofluvial materials that comprise the area's aquifer. Agriculture there (irrigated vegetable rotation, irrigated and nonirrigated corn and hay, dairy) loses large amounts of NO_3-N (100-150 kg ha^{-1} yr^{-1}) and pesticide residues to groundwater (Kraft and Stites, 2003; Kraft et al., 1999). Salient conclusions from the Stockton Study Area were:

- Groundwater in the Stockton Study Area was mostly of recent origin, dominantly 1985 and younger.
- Nitrate-N usually exceeded the drinking water MCL and Wisconsin Enforcement Standard of 10 mg L^{-1}, averaging 20 mg L^{-1} and ranging 4.4 to 41 mg L^{-1}.

- Nitrate was conserved, i.e.,denitrification was not appreciable.
- Residues of five pesticides were detected: atrazine, alachlor, metolachlor, metribuzin, and pendamethalin. Alachlor and metolachlor residues were most prevalent (mainly the OA and ESA degradates), and atrazine degradates were also common.
- Summed pesticide residues in individual wells were typically 5 to 15 μg L^{-1}, but reached up to 42 μg L^{-1}.
- Modern concentrations of NO_3 and pesticide residues had penetrated most of the study area aquifer, hence aquifer pollutant loads were substantially in equilibrium with current land uses.

In contrast, Springfield Corners soils are deep silt loams, more able to hold and cycle moisture, nutrients and pesticides than in Stockton. The aquifer is thick, and covered by about 30 m of medium textured till. Farming involves grain, forages, and dairy, with fewer fertilizer and pesticide inputs

STUDY AREA

Setting

The Springfield Corners study site (Figure 2) is located in northwest Dane County Wisconsin, approximately 1 km southeast of the Village of Springfield Corners. The site is in the western part of the Six Mile and Pheasant Branch Creeks watershed (LR10-012). Surface water drains east, eventually discharging into Lake Mendota, the Yahara River, and then the Rock River. The site is close (about 2 km) to the topographic divide with the Black Earth Creek watershed, west of which surface water discharges to the Wisconsin River. The area lies on hummocky glacial topography with slopes that range up to about 20%. The climate is humid, temperate, and continental (Glocker and Patzer, 1978), with cold and snowy winters and warm summers. The average frost-free growing season is 176 days. Annual precipitation averages about 770 mm, with about 55% of that falling in May through September. Groundwater recharge in the vicinity has been estimated at about 125 mm yr^{-1} (Bradbury et al., 1997).

Farming is dominated by dairy production and cash grain. Fields are usually planted to field corn, soybean, and hay crops. Agriculture has profoundly impacted groundwater quality in the area. For the South Central Agricultural Statistics reporting district (which includes the Springfield Corners area), drinking water wells had a 22% NO_3 drinking water standard exceedence rate ("maximum contaminant level," or MCL), and a detection rate of atrazine, alachlor, and metolachlor residues of 32-38%, 36-64%,
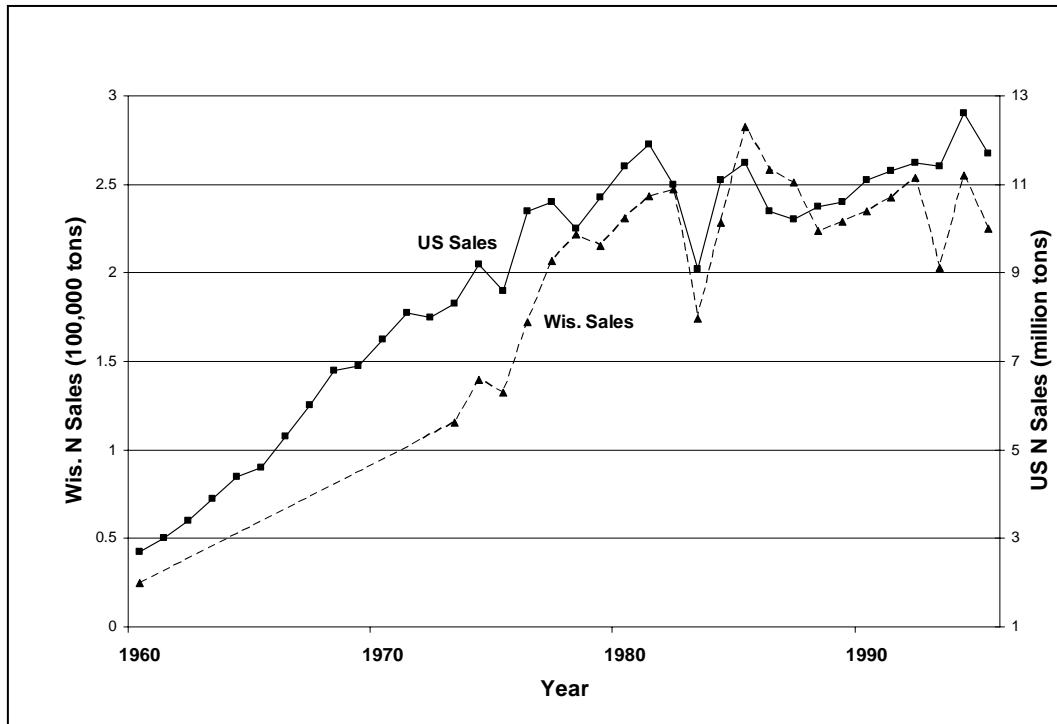
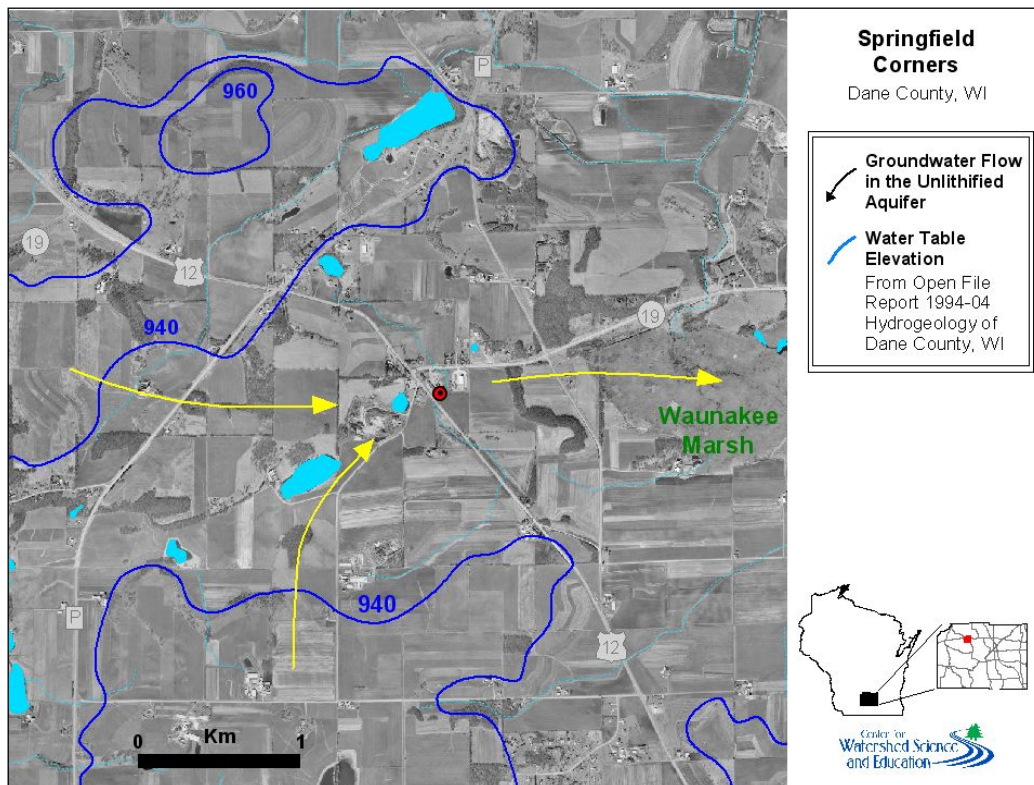Figure 1. Increase in US and Wisconsin fertilizer-N since 1960 (compiled from various USDA sources).

Figure 2. Location, features, and groundwater flow patterns in the Springfield Corners area.

7

and 40%, respectively (LeMasters and Baldock, 1995; Vanden Brook et al., 2002).

The geology consists of Pleistocene sediments overlying Cambrian and Precambrian rock. Pleistocene sediments (Horicon Member of the Holy Hill Formation) are dominantly a gravelly, clayey, silty, sand till (Clayton and Attig, 1997). Well-drained silt loam soils cap the Pleistocene sediments (Glocker and Panzer, 1978). Bedrock is typically encountered about 30 m below grade, though outcrops sometimes occur on sideslopes. Rock formations (upper- to lower-most) consist of Tunnel City sandstone, Wonewoc sandstone, Eau Claire shale, Mount Simon sandstone, and unnamed Precambrian crystalline rocks. Krohelski et al. (2000) estimated a county-scale average hydraulic conductivity for the till of 10^{-5} m s^{-1}. The Tunnel City and Wonewoc are grouped as the "upper bedrock aquifer" (Bradbury et al., 1999; Krohelski et al., 2000), for which hydraulic conductivity has been estimated at $10^{-4.8}$ m s^{-1}. The upper bedrock aquifer is well connected to surficial hydrologic processes. The Eau Claire in this vicinity is a shaley confining unit and has a substantially lower (but not precisely known) conductivity than the other rock units. The Mount Simon comprises the "lower bedrock aquifer," with an estimated hydraulic conductivity of $10^{-4.5}$ m s^{-1}. The Mount Simon is relatively isolated from surficial processes, and contains much older groundwater than that of the upper bedrock aquifer, on the order of many decades to perhaps to one or two centuries (K. Bradbury, pers. comm.).

Study Site

The study site consists of three monitoring wells and one deep borehole located at the Dane County Highway Department facility at the southeast corner of the US Highway 12 and Wisconsin Highway 19 intersection (Figures 2 and 3). The property is approximately four acres and contains several buildings used for highway equipment maintenance, refueling, and asphalt and salt storage. All road materials are presently stored in covered buildings, but outdoor salt storage is known to have occurred in the past. Road salt impact on shallow groundwater was expected from past storage practices and present winter deicing operations on adjacent highways. The monitoring wells and borehole are at the southernmost edge of the property. The surrounding area consists mostly of agriculture in row and forage crops.

The study site was previously used in the work of Krohelski et al. (2000) and Bradbury et al. (1999). The thicknesses of the geologic units are: till - 44 m; Tunnel City - 17 m; Wonewoc - 40 m; Eau Claire - 14 m; Mount Simon - about 60 m. The three monitoring wells were installed as part of this study,

and have 1.5 m long screens that terminate at 24.3, 30.5, and 38 m depths. The deep borehole was installed previously (1993) for the studies of Bradbury et al. (1999) and Krohelski et al. (2000). It is cased through its upper 47 m, and then open to 142 m, penetrating 26.5 m into the Mt. Simon.

We estimated a site-specific hydraulic conductivity for the till of about 10^{-7} m s^{-1} from a bail down test, substantially smaller than the Dane County average reported by Krohelski et al. (2000). A strong downward gradient (about 0.15) was also observed in the till. The strong gradient and large hydraulic conductivity contrast between the till and upper bedrock aquifer indicates that flow in the till was mainly vertical (e.g., Freeze and Cherry, 1979; p. 197). This supports an operating hypothesis that till groundwater at the site currently originates from within a few tens of meters of the monitoring wells. Groundwater in the upper bedrock aquifer originates as diffuse precipitation recharge from an area within 2-3 km of the study site (Figure 2; Krohelski et al., 2000) and flows east, discharging to surface water at indefinite locations within the watershed. Groundwater in the lower bedrock aquifer flows west. The Eau Claire shale was an effective barrier between the upper and lower aquifers, as evidenced by a 15 m head drop across the shale when the deep borehole was first installed (Bradbury et al., 1999). However, its installation has perturbed vertical flow patterns in its vicinity (Figure 4), and allows groundwater in the upper bedrock aquifer to intrude into the lower. In addition, we speculate that aquitard breaching lowered hydraulic heads in the vicinity of the borehole and caused a reversal in flow direction in the till (Figure 4).
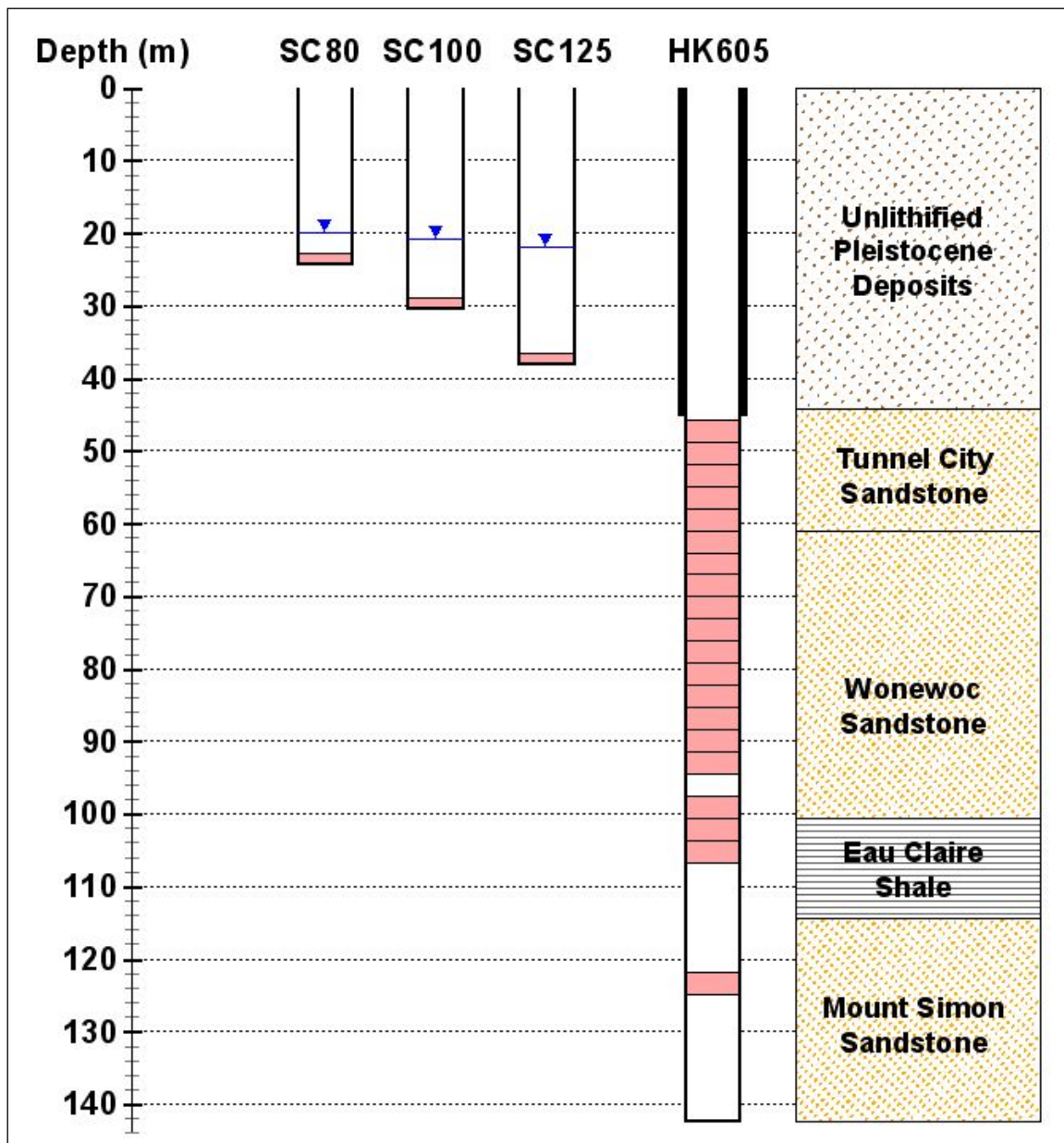
Figure 3. The geology and instrumentation of the Springfield Corners site. Instrumentation consisted of three standard monitoring wells and one deep borehole. Shaded areas are well screens or borehole intervals sampled for the study.
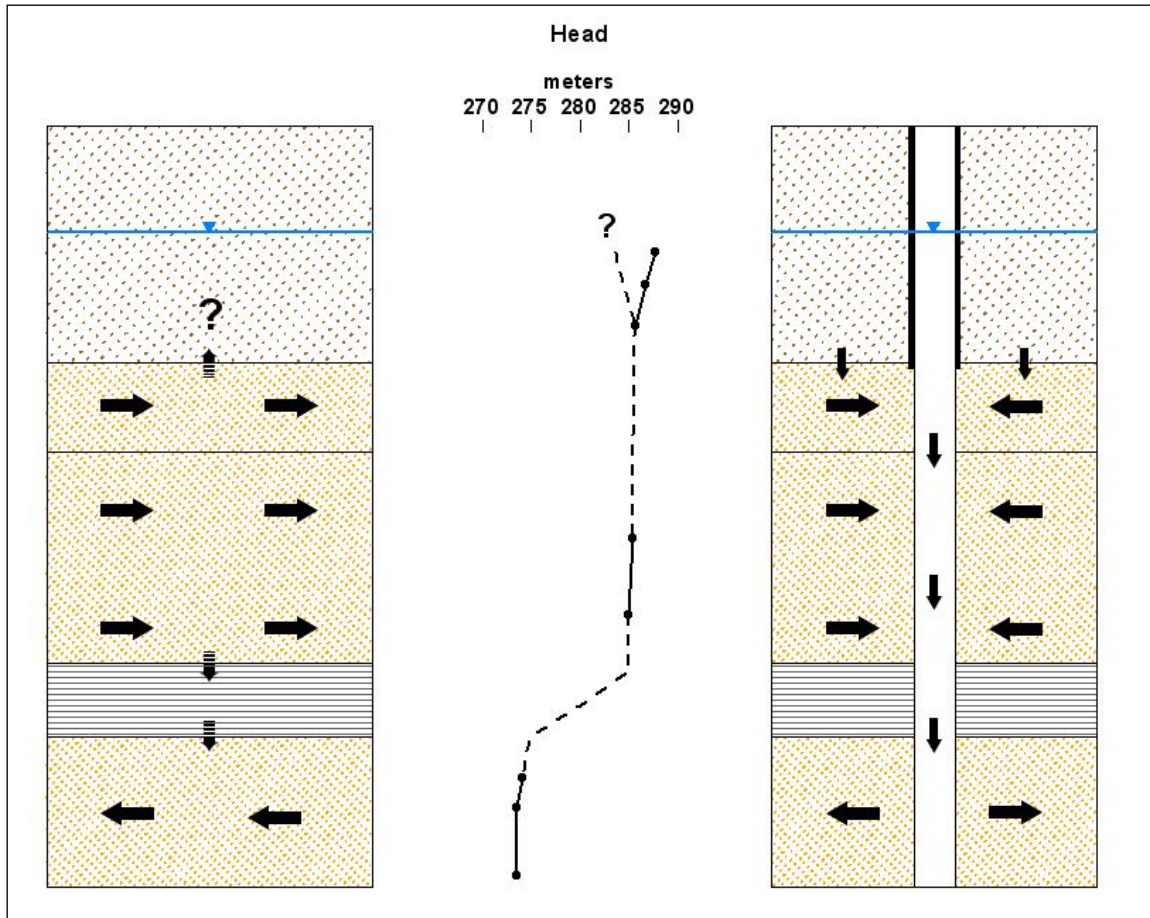
Figure 4. Groundwater flow and head conditions at the Springfield Corners study site. Before the installation of the deep borehole in 1993 (left), regional flow patterns predominated. We speculate that the till may have been a confining unit. Since borehole installation (right), local groundwater drains into the upper borehole and out of the lower. Head patterns (center) are for conceptual purposes only, based on a few measurements on multiple dates. Note large head loss across the Eau Claire shale. Dashed lines indicate inferred patterns

11

METHODS

This study relies on a premise that groundwater pollutant loading and fate history are retained in the spatial structure of an aquifer. Loading and fate information can be extracted by acquiring samples from a groundwater flow system and subjecting them to groundwater dating and other appropriate analyses (e.g., Bholke and Denver, 1995). This information in turn can indicate the degree that an aquifer is in pollutant equilibrium with modern land management practices. An aquifer whose saturated thickness has been completely penetrated by modern water and pollutants (or their byproducts) would be in equilibrium with modern management practices, while a partially penetrated aquifer would not. In partially penetrated aquifers, average water quality would be expected to deteriorate over time and pollutant load and export would be expected to increase, until penetration is completed.

Conceptual Model of Hydrologic Systems and Pollutant Loading

Our conceptual model is that the study area groundwater system behaves in accordance with the groundwater hydraulics described by King (1899) and Hubbert (1940) (Figure 5). That
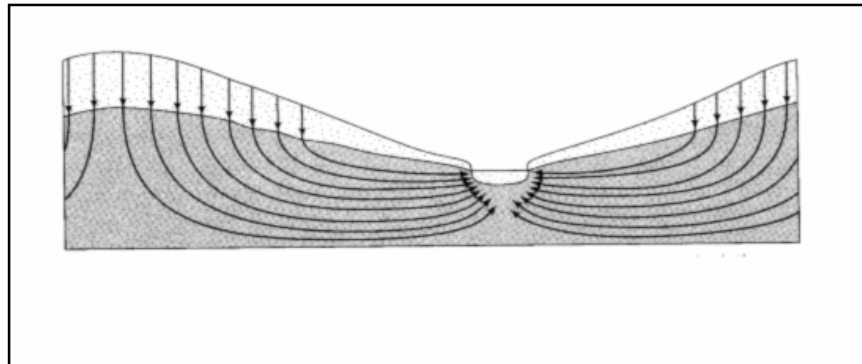
Figure 5. Illustration of groundwater flow patterns following King (1899). From Domenico and Schwartz, 1998.

is, the groundwater flow system is unconfined, receives areally-distributed recharge, and naturally discharges at line sinks (streams) or point sinks (wetlands, springs). In such systems, younger water generally overlies older water, with oldest water being deep and near discharge zones. Further, the conceptual model holds that NO_3 and pesticides originate as a diffuse source across the landscape, and that NO_3 loading history proceeded in three periods. In the pre-settlement period, NO_3 loading to groundwater was relatively small; the ecological system that prevailed on the landscape efficiently

scavenged available N and incorporated it into soil-plant systems, lost NO_3 to the atmosphere by dentirification. Nitrate loading to groundwater was small compared to groundwater denitrification capacity. In the post-settlement period, natural ecosystems were converted to agro-ecosystems. Cultivation initially resulted in a large release of N from soil organic matter oxidation, some of which was taken up by plants, but some that leached to groundwater. This release was at first rapid but then slowed, as the more labile organic matter was depleted, but still persists in modern times (Oberle and Keeney, 1990; Meisinger and Randall, 1991). During this period, N-fixing crops and increased livestock densities also proliferated. Nitrate loads to groundwater still may have been small enough to be substantially eliminated by available groundwater denitrification capacity. The third and present loading period began about 40 years ago with the introduction and large increase of chemical fertilizer N and pesticide applications to the landscape. Though fertilizer-N and pesticide use leveled in the mid-1980s (Figure 1), agricultural area aquifers are probably continuing to accumulate pollutants because groundwater residence times tend to be longer than the chemical fertilizer and pesticide use period, unless denitrification and degradation are limiting.

Sampling Procedures

The deep borehole was sampled in June 2003 and three monitoring wells were sampled in October 2003. Monitoring wells were purged (three standing volumes or until dry) and sampled using an inertial pump (Waterra, Inc.) fitted with a 12 mm diameter copper drop pipe attached to a stainless steel foot valve. To sample the deep borehole, we utilized a straddle-packer to isolate discrete intervals. Twenty intervals were sampled; 17 in the upper bedrock aquifer, two in the upper part of the Eau Claire, and one in the Mount Simon. We attempted to sample two other intervals in the Eau Claire, but insufficient yield precluded sample collection. The straddle-packer rig consisted of a 5.4 m long, 100 mm diameter steel pipe with 1.2 m long neoprene packers on each end. This configuration isolated 3-m formation intervals. A 150 mm by 50 mm hole cut in the center of the pipe served as a screen. This screening arrangement reduced water contact and possible contamination from the neoprene packers. A submersible electric pump enclosed in the steel pipe delivered water to the surface. Packers were inflated with nitrogen. Isolated intervals were purged of 2000 L of water at a rate of 2 L s^{-1} prior to sampling. The pump rate was slowed using a gate valve to about .2 L s^{-1} for sample acquisition. During pumping, pressure transducers within and outside the sample interval were monitored for leakage.

Samples for inorganic and pesticide analysis were collected using routine protocols (WDNR, 1996; http://dnr.wi.gov/org/water/dwg/gw/pubs/GW-SFM.PDF) for well purging, sample collection, filtering, and preservation as appropriate for individual analytes. Field measurements (temperature, pH, specific conductance, and total dissolved gas pressure) were obtained using a YSI 650 DMS sonde and a Common Sensing total dissolved gas pressure (P_T) monitor. Both instruments were equipped with flow cells to avoid exposure of sample to the atmosphere during measurement.

Dissolved gas samples were obtained by pumping induced ebullition (PIE; Browne, 2004). Groundwater was sampled by placing PIE apparatus induction tubes about 1.5 m down the drop pipe into the monitoring well or packer apparatus. While the drop pipe was allowed to continuously overflow, a portion of the flow was diverted into the PIE apparatus. During the process, a nominal gas yield of .02 mL s^{-1} was achieved at a water induction rate of 6 mL s^{-1}. Replicate gas samples (n=3) for CFC age-dating measurements (CFC11, CFC12, CFC113) were collected from the PIE apparatus into a 25 mL plastic syringe and transferred into evacuated 15 mL serum bottles. A total of 60 mL of harvested gas at atmospheric pressure was compressed into the serum bottles. Replicate gas samples (n=2) for other dissolved gases (Ar, N_2, O_2, CO_2, N_2O, CH_4) were collected and stored similarly.

Analytical Procedures

Inorganics

Metals (Al, Ca, Mg, K, Na, Mn, Fe), Si, and S (reported as SO_4) were analyzed by inductively coupled plasma AES (APHA, 1995 methods 311B, 3111D, and 3129 B). Chloride, NO_2+NO_3-N, NO_2, NH_4, and total Kjeldahl N (TKN) were analyzed using automated colorimetry. ANC (acid neutralizing capacity) was analyzed by titration (APHA, 1995; method 2320B). DO was analyzed by the Winkler method (APHA, 1995; method 4500-O-B). These analyses were run at the University of Wisconsin - Stevens Point WEAL facility, which is State of Wisconsin certified for these analyses. The median charge balance error (Freeze and Cherry, 1979) was 3.5%, and ranged -0.62-15%. Error was usually associated with missing anionic charge, and larger errors were associated with greater ion concentrations. Past experience has indicated missing ANC is the most likely cause (e.g., Kraft et al., 1999). Hence, we report both a measured and calculated ANC, as the difference between summed cations and summed noncarbonate anions (e.g., Stumm and Morgan, 1996). Finally, we report "summed ion concentration," a surrogate for total dissolved solids, which we calculated as the sum of ion concentrations plus the bicarbonate concentration, which was determined from ANC.

Pesticide residues

        Atrazine, atrazine metabolites, and other parent herbicide residues were analyzed by GC/MS (modified EPA method 8270) at the WEAL facility with an extraction method developed by the Wisconsin State Laboratory of Hygiene to isolate the more water soluble atrazine metabolites. WEAL is state certified to analyze these residues. Chloroacetanilide herbicide metabolites were determined using solid-phase extraction and high performance liquid chromatography/diode array detection as described by Zimmerman et al. (2000). Approximately 60% of the samples were confirmed by liquid chromatography/mass spectrometry at the Wisconsin Department of Agriculture, Trade and Consumer Protection's Bureau of Laboratory Services or the Syngenta Crop Protection Laboratory.

Dissolved Gases

        Mole fractions (X_i) of individual gases within gas samples were determined by gas chromatography. A pulse discharge detector (PDD) in the helium ionization mode (Wentworth et al., 1994) was used to detect N_2, Ar, O_2, N_2O, CO_2, and CH_4; a ^{63}Ni electron capture detector (N_2 carrier gas) was used to detect CFCs (CFC11, CFC12, CFC113). Helium was the carrier gas for all PDD measurements; other chromatographic conditions (columns, temperatures, carrier gas flow rates) were similar to those described in McMahon et al. (2000) for N_2, Ar, and O_2, for CH_4, CO_2 and N_2O, and in Busenberg and Plummer (1992) for CFC11, CFC12, and CFC113.

        Gas standards and samples were injected into the GC using a gas sample loop on a ten-port valve. Six point calibration curves (mole fraction versus peak area) were performed by injection of gas dilutions prepared by mixing aliquots of blank gas and standard gas. In load position, the sample loop was maintained at ambient lab temperature and pressure prior to injection.

        Partial pressures (P_i) of individual gases within the groundwater samples were determined by:

$$P_i = X_i\, P_T\, /\, F_i$$

where P_T is the total dissolved gas pressure measured in the field and F_i is an analyte-specific fractionation coefficient reported in Browne (2004). Concentrations (C_i) of individual dissolved gases were determined using Henry's Law:

$$C_i = K_{Hi}\, P_i$$

where K_{Hi} is the Henry's Law constant calculated for the field temperature from temperature dependent solubility data reported in Busenberg and Plummer (1992, CFCs) or Wilhelm et al. (1977, all other gases).

Denitrified N

Dissolved N_2O-N, and dissolved N_2-N in excess of atmospheric concentrations ("denitrified N_2-N"), were used to account for denitrified NO_3. Denitrified N_2-N was quantified (Heaton, 1981; Martin et al., 1995) using the following Henry's Law relationship:

$$\text{Denitrified } N_2\text{-N} = C_{N2} - (K_{H,N2,r} \, P_{atm,N2})$$

where C_{N2} is the total concentration of dissolved N_2, $P_{atm,N2}$ is the partial pressure of N_2 in the atmosphere, and $K_{H,N2,r}$ is Henry's Law constant calculated for the temperature during groundwater recharge. Argon was used as a non-biogenic, atmospheric reference gas concentration to determine the temperature of groundwater during recharge.

CFC Age Date Assignments

Due to solubility of gases within atmospheric moisture, CFCs have accumulated in the hydrosphere in conjunction with their accumulation in the atmosphere. Because their rapid atmospheric accumulation has been well documented from about 1940 to the present and because detection at part per trillion concentrations is possible using common laboratory instrumentation (GC ECD), CFCs have become valuable tracers for groundwater recharge age-dating (Busenberg and Plummer, 1992; 2000; Puckett et al., 2002). The premise of CFC age-dating is that the dry-gas mole fraction of CFCs within the gases dissolved in groundwater reflects the atmospheric mixing ratio (dry air mole fractions) of CFCs during the year of groundwater recharge (Appendix IV).

The mole fractions of CFC11, CFC12 and CFC113 measured within the gas harvested from groundwater, adjusted to the temperature of groundwater recharge using Henry's Law relationships, were compared to historic records of CFC atmospheric mixing ratios (Appendix IV) to determine the year of groundwater recharge (the "apparent CFC recharge age-date"). The minimum age-date estimate of each CFC was bounded by its practical laboratory detection limit. The practical detection limits were: CFC 11 - 4 pptv (parts per trillion by volume); CFC 12 - 9 pptv; CFC 113 - 1.3 pptv. These correspond to the following minimum age-dates: CFC 11 - 1955; CFC 12 - 1951; CFC 113 – 1959. For CFC 11 and CFC 113, the atmospheric-mixing ratio vs. time curve flattens substantially and then falls between about 1990 and present. Hence, a given atmospheric-mixing ratio does not correspond to a unique age-date. Therefore, we report an age-date of 1995 for CFC 11 and 113 samples with atmospheric-mixing ratios corresponding to 1990 to 2001, recognizing an uncertainty of about $\pm$ 5 years.

CFC 11, 12, and 113 yield up to three independent observations of apparent age for each groundwater sample. However, agreement of all observations is not usually attained unless conditions are ideal. The most frequent conditions causing disagreement include:

1. Nonatmospheric sources of CFCs (e.g., pesticide carrier matrix) lead to a concentration in groundwater in excess of equilibrium with the atmosphere at the time of recharge (Busenberg and Plummer, 2000). These samples are deemed "environmentally contaminated."

2. Biological degradation of one or more CFCs (in order of susceptibility CFC11 >> CFC113 > CFC12) under reducing conditions causes an older apparent age for CFC11 than CFC113 and CFC12, a lower concentration of CFC113 than CFC12, or both.

3. Mixing of ground water (shallow and deep) containing different relative mixing ratios of the four indicator gases produces, for example, a younger apparent age-date by CFC113 than by CFC12. This tends to be a fairly subtle and complex condition, requiring somewhat subjective speculation. As a practical matter, we did not consider it in our data analysis.

A "best" apparent age-date for each water sample based on the following guidelines (modified from the United States Geological Survey; http:\\water.usgs.gov\lab\dissolved-gas):

1. Any observation with a ground water concentration in excess of that in equilibrium with the modern atmosphere was considered environmentally contaminated and therefore invalid. These occurrences are left blank in Table 2.

2. Under reducing conditions (operationally defined by $DO < 1$ mg L^{-1}), when substantial disagreement existed between two or more CFCs, the most stable (least susceptible to biological degradation) was selected as the valid observation. In this hierarchy CFC12 trumps both CFC113 and CFC11 and CFC113 trumps CFC11. Observations invalidated on this basis are indicated in gray in Table 2.

3. Under nonreducing conditions, when disagreement existed among two or more CFCs, one or two CFCs providing the oldest apparent age-date were selected as valid observations. The excluded CFCs were deemed environmentally contaminated.

4. Where near agreement among multiple age-dating gases was evident, the observations were averaged.

In this study, CFC12 measurements appeared unreliable compared to CFC11 and CFC113. Whereas eight CFC12 observations appeared to be environmentally contaminated (rule 3) beyond atmospheric equilibrium, only three CFC11 observations and no CFC113 observations were. All common CFC11 and CFC113 age dates agreed well, but only two CFC12 measurements did. Hence, in most instances, we rejected CFC12 age date estimates (Table 2).

RESULTS AND DISCUSSION

The sampling procedure yielded three samples from the till, 17 from the upper bedrock aquifer, two from the Eau Claire, and one from the lower bedrock aquifer. The samples obtained from the Eau Claire and the lower bedrock aquifer (bottom three intervals in Figure 3) bore chemical signatures (inorganic, pesticides, and dissolved gasses) indicative of upper borehole groundwater (Appendix II). This connotes that, as expected, water drained from the upper part of the borehole and displaced native water in the lower. Hence, we rejected the samples from the Eau Claire and lower bedrock aquifer as being unrepresentative of native conditions. The remainder of this report deals only with the samples taken from the till and upper aquifer units.

Inorganic Analyses

The groundwater chemistries of the till and upper bedrock aquifer (Table 1 and Appendix III) differed greatly. Till groundwater had double the concentration of summed major ions (1015-1688 mg L^{-1}; Figure 6), and was especially enriched in Na and Cl that we attribute to pollution from road salt. Till groundwater also contained less dissolved oxygen (DO; 2.5-4.7 mg L^{-1}), more dissolved organic carbon (DOC), and slightly elevated Fe and Mn relative to the upper bedrock aquifer. Despite the slightly elevated Fe and Mn, oxidizing conditions were indicated by DO concentrations and elevated NO_3-N (13-19 mg L^{-1}).

Upper bedrock aquifer groundwater was the Ca – Mg – HCO_3 type (Table 1) with summed ion concentrations of 434-798 mg L^{-1}. Major ions decreased with depth (Figure 6). The median pH, ANC, and DOC were 7.4, 6.7 meq L^{-1}, and 0.48 mg L^{-1}. The relative abundance of cations remained constant with depth, with Ca and Mg comprising about 50% and 44% of cationic charge. Anionic charge was dominated by HCO_3, but its relative importance was depth dependent. HCO_3 made up 82% of anionic charge at the top of the upper bedrock aquifer, but 97% at the bottom. The cause was larger Cl concentrations in the upper part of the profile compared to the lower (Figure 7). Groundwater was well oxygenated (median DO = 6.5 mg L^{-1}) at all depths, and other indicators of reducing conditions (e.g., elevated Fe and Mn) were mostly absent.

19

Table 1. Summary of groundwater analyses in the till and upper bedrock.

Analyte	Upper Bedrock Aquifer (n = 17)				Till (n = 3)			
	Mean	Median	Max	Min	Mean	Median	Max	Min
	------- mg L^{-1}, except ANC (meq L^{-1}) and pH -------							
Ca	76.6	71.0	101.7	58.0	100.9	108.0	117.4	77.4
Mg	40.4	38.6	53.9	30.2	59.8	66.8	67.6	44.9
Na	8.6	7.0	18.4	3.7	197.4	214.0	255.0	123.3
K	2.4	2.5	4.1	1.3	3.5	3.5	3.7	3.4
NO_3-N	5.7	4.3	13.2	0.9	15.4	13.6	19.1	13.4
Cl	22.6	8.5	56.5	3.0	236.7	246.0	385.0	79.0
SO_4	15.6	15.7	22.9	4.1	31.7	31.6	31.8	31.6
pH	7.4	7.4	7.6	7.2	7.4	7.3	7.7	7.1
O_2	5.7	6.5	7.3	2.2	3.9	4.5	4.7	2.5
Fe	0.008	0.006	0.055	<.001	0.100	0.123	0.148	0.028
Mn	0.001	0.001	0.003	<0.0001	0.040	0.045	0.050	0.025
Summed ions	585	555	798	434	1361	1381	1688	1015
Organic C	0.5	0.48	0.8	0.32	3.8	3.3	5.7	2.4
Measured ANC	6.2	6.1	7.3	5.3	8.0	7.9	8.3	7.8
Calculated ANC	6.7	6.5	7.9	5.2	10.8	9.7	15.4	8.4
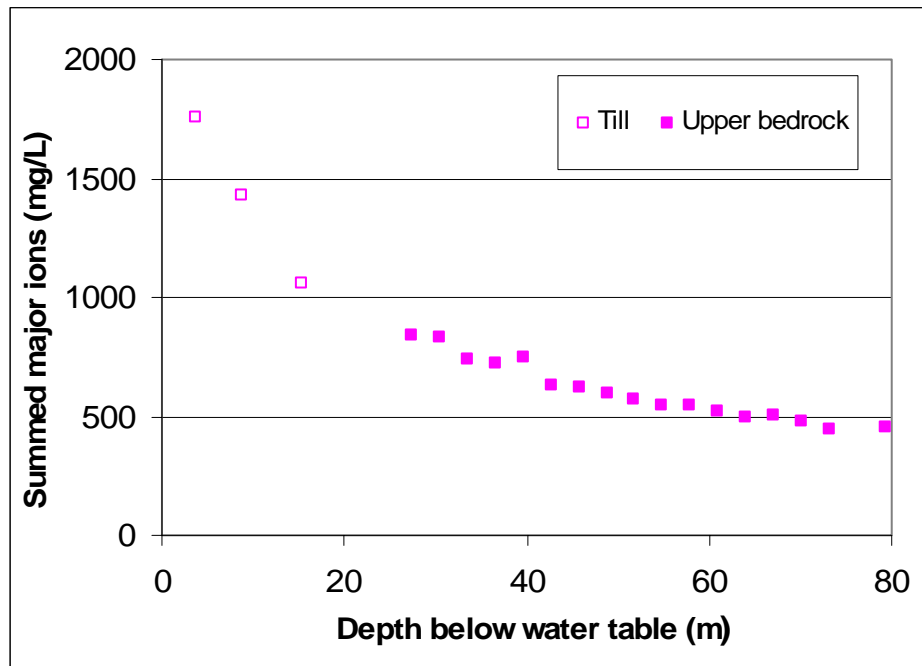
Figure 6. Sum of ions with depth below water table in the till and upper bedrock aquifer units.
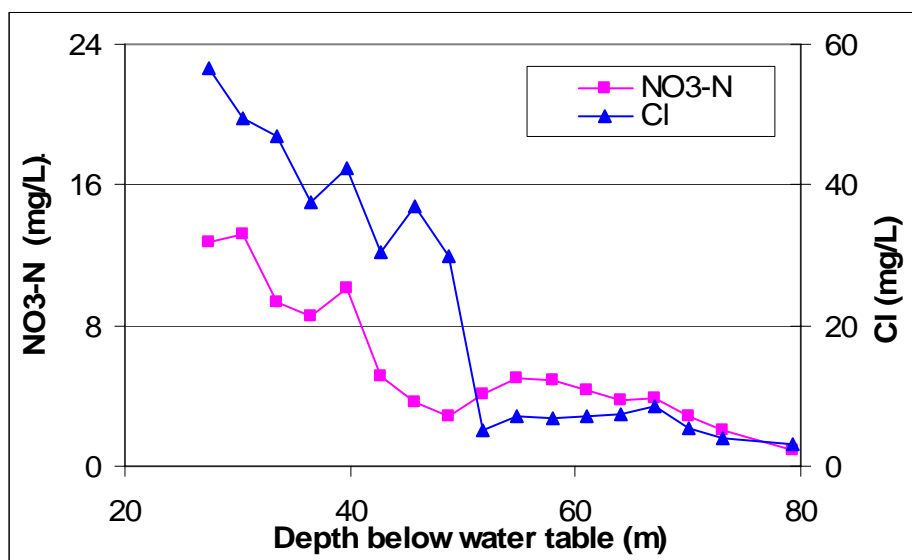
Figure 7. Decline in NO_3-N and Cl with depth in the upper bedrock aquifer.

Groundwater Age Dates

CFC-based age dates could be inferred for all except one of 20 samples (Table 2). (Sample vial breakage precluded analysis of the one.) CFC11 and CFC113 provided age-date information on 16 and 19 samples, respectively, and agreed well, with a mean difference of only 1.2 years. CFC12 provided younger apparent ages (about 11 years on average) than CFC 11 and CFC 113. Because all three CFCs are relatively resistant to biological degradation under nonreducing conditions, we attribute this discrepancy to environmental CFC12 contamination, as discussed in "Methods." Hence, we have discarded CFC 12 age-dates as unreliable.

Groundwater in the till yielded age-dates of 1977-1986, and groundwater in the upper bedrock aquifer yielded age-dates of 1963-1985 (Figure 8). Groundwater age declined smoothly with depth in the upper bedrock aquifer, at a rate of about 0.4 yr m^{-1}. Notably, groundwater age dates increased with depth in the till (i.e., deeper groundwater was younger), at a rate of about 0.76 yr m^{-1}. A number of postulates could be advanced to explain this behavior, for instance, that three-dimensional preferential flow paths in the till allowed younger water to bypass some strata; or that aquitard breaching lowered hydraulic heads in the vicinity of the borehole and reversed vertical flow direction in the till (see Study Area).

21

Table 2. Results of age-date analyses with depth below water table. Blanks cells were environmentally contaminated. Gray cells were deemed invalid (see Methods).

Depth below water table (m)	CFC11	CFC12	CFC113	Best
3.7			1977	1977
8.8			1982	1982
15.3			1986	1986
27.4	1985	1994	1983	1984
30.5	1986	1991	1984	1985
33.5	1979		1980	1979
36.6	1974	1987	1976	1975
39.6	1979	1994	1980	1979
42.7	1970		1973	1971
45.7	1969		1970	1969
48.8	1972		1971	1972
51.8	1972		1969	1970
54.9	1970	1988	1968	1969
57.9	1969	1986	1968	1968
61.0	1968	1980	1963	1965
64.0	1968	1974	1962	1965
67.1	1968	1972	1966	1967
70.1	------- no analysis --------			
73.2	1965	1964	1961	1963
79.2	1965	1963	1963	1964

Nitrogen

Nitrate-N and denitrified N_2-N were the dominant dissolved N forms (Table 3) in both the till and upper bedrock aquifer. N_2O was negligible as a fraction of dissolved N, but perhaps present at concentrations of consequence as a greenhouse gas. Till groundwater contained 13-19 mg L^{-1} NO_3-N and 0.7-1.9 mg L^{-1} denitrified N_2-N. NH_4-N was negligible, but TKN ranged 0.4-1.2 mg L^{-1}. In the upper bedrock aquifer, NO_3-N was 13.2 mg L^{-1} at the top of the unit and declined to 0.9 mg L^{-1} at its base (Figure 9). The upper 17 m of the 57 m thick aquifer exceeded the 10 mg L^{-1} NO_3-N MCL and Wisconsin Groundwater Enforcement Standard. Nitrate-N concentrations increased linearly over time, at a rate of 0.5 mg L^{-1} yr^{-1} ($r^2 = 0.90$; Figure 10), and crossed a threshold in 1979 whereby incoming recharge began to exceed the MCL. Nitrate trends showed no signs of leveling. Chloride trends paralleled those of NO_3 (Figure 10), except that Cl jumped abruptly in 1970.

Table 3. Summary of N analyses.

| N Analysis	% Detects	Detection Limit	Minimum	Median	Maximum
		-------------- mg L^{-1} N -----------------			
		---------- Till -----------			
NO_3+NO_2	100	0.1	13.4	13.6	19.1
Total Kjeldahl	100	0.07	0.43	0.99	1.24
NH4	100	0.01	0.4	0.1	0.19
Denitrified N_2	100	0.2	0.7	1.2	1.8
N_2O	100	0.001	0.0004	0.00047	0.00053
		---------- Upper bedrock aquifer -----------			
NO_3+NO_2	100	0.1	0.9	4.3	13.2
Total Kjeldahl	76	0.07	0.07	0.11	0.58
NH4	76	0.01	0.19	0.044	0.08
Denitrified N_2	100	0.2	1.5	2.9	4.6
N_2O	100	0.001	0.0031	0.005	0.016
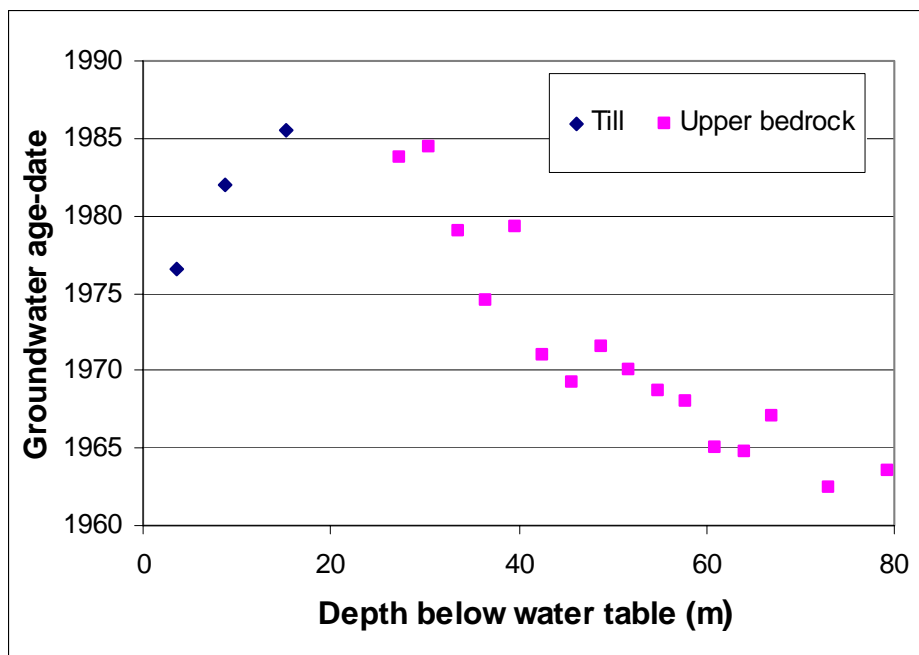
Figure 8. Groundwater age dates with depth in the till and upper bedrock aquifer.
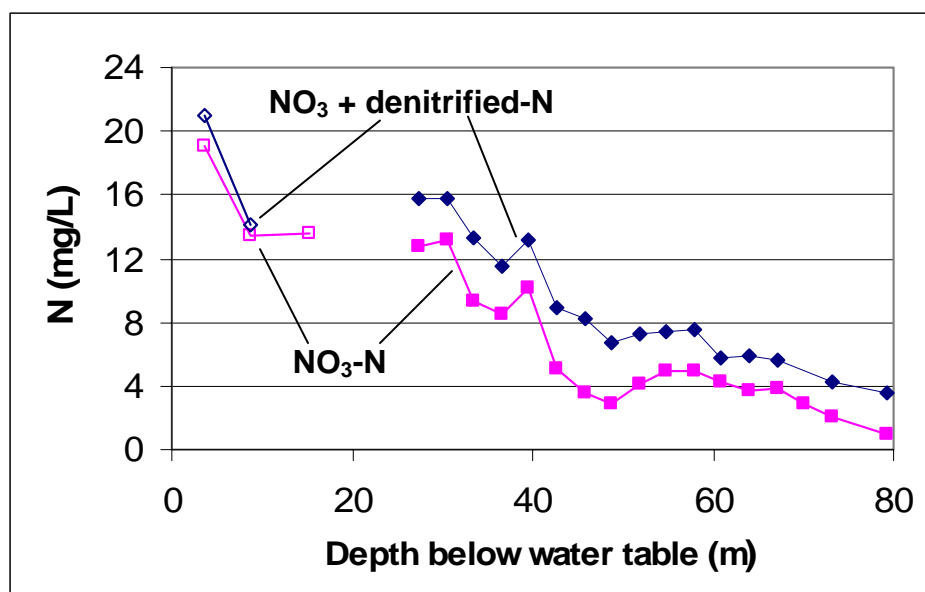
Figure 9. Nitrate-N and NO_3 plus denitrified N_2-N in the till (open symbols) and upper bedrock aquifer (closed symbols).
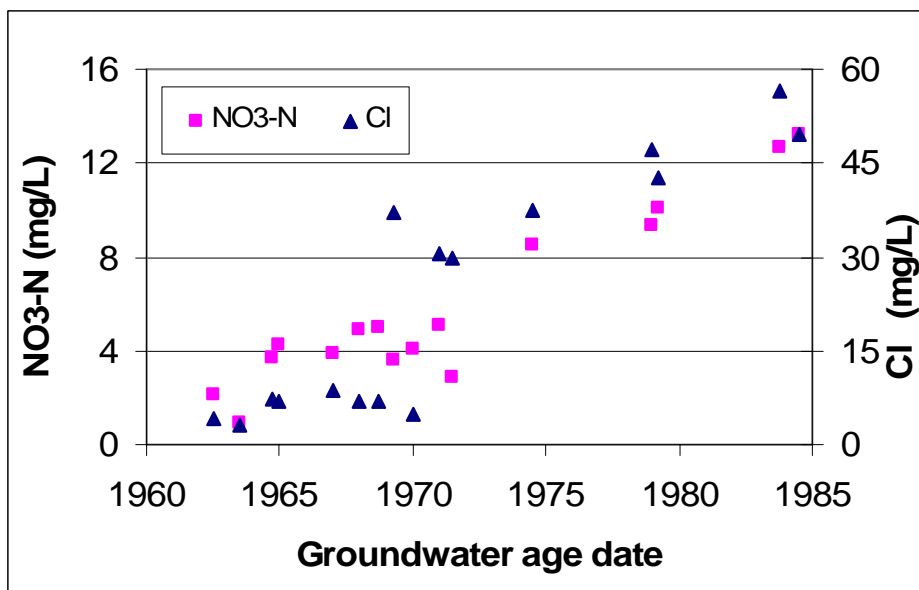
Figure 10. Nitrate-N and Cl with age-date in the upper bedrock aquifer.

This may indicate that the same land management changes that brought about increased N leakage to groundwater also brought about a large increase in Cl. Perhaps fertilizer mixtures that incorporated both N and KCl were responsible. Denitrified N_2-N was remarkably constant in the upper bedrock aquifer, averaging 2.9 mg L^{-1} (Table 3). Because of this consistency, denitrification was relatively more effective in removing NO_3-N when loads were smaller. In the deepest part of the aquifer associated with early 1960s groundwater, denitrification eliminated 73% of the groundwater's original NO_3 load, but only about 16% of the load in shallow parts of the aquifer associated with 1980s groundwater.

Pesticide Residues

Detected pesticide residues were alachlor ESA, metolachlor ESA, and atrazine with its deethyl-, deisopropyl-, and diamino- degradates. No detections were observed of alachlor, alachlor OA, metolachlor, metolachlor OA, nor many other pesticide residues potentially detectable by the analytical methods used in this study. In the till, summed pesticide residues ranged up to 4 µg L^{-1} (Figure 11; Table 4). Atrazine residues were absent and alachlor ESA and metolachlor ESA concentrations were similar to those in the top part of the upper bedrock aquifer (Figure 11; Table 4). In the upper bedrock aquifer, summed residue concentrations ranged up to 2.5 µg L^{-1}. Atrazine residues ranged from undetectable

(0.09-0.2 µg L^{-1}) to 0.48 µg L^{-1}, substantially less than the Wisconsin Enforcement Standard of 3 µg L^{-1}. Atrazine residue detections were small compared with much of south central Wisconsin (e.g., VandenBrook et al., 2002). Parent atrazine was found in the most groundwater samples (10 of 20), deethyl-atrazine in five samples, deisopropyl- in one, and diamino- in none. Alachlor ESA was commonly detected in the till and upper part of the upper bedrock aquifer, at typical concentrations of 1.0-1.5 µg L^{-1}. Metolachlor ESA detections were small and relatively constant (0.3-0.4 µg L^{-1}) in the upper bedrock aquifer.

Pesticide residues decreased with depth but penetrated the upper two-thirds of the upper bedrock aquifer (Figure 11). Summed pesticide residue concentrations increased with NO$_3$ (Figure 12), and varied with groundwater age date (Figures 13 and 14). The earliest age date that residues were detected corresponded well to the estimated first year of use of the parent compound in Wisconsin (atrazine - 1961; alachlor - 1970; metolachlor - 1978; Nehring and Grube, 2004). Both summed atrazine residues and alachlor ESA were detected sporadically and at relatively low concentrations after initial detection, and then increased around age date 1975. Atrazine residues were 0.34-0.48 µg L^{-1} in 1975-1986 groundwater, and alachlor was 1.2-1.6 µg L^{-1}. Metolachlor had a different pattern, appearing first in 1975 and then remaining 0.3-0.4 µg L^{-1}.

Does the residue concentration - time pattern (Figures 13 and 14) provide evidence for either residue degradation or recalcitrance? Given a temporally constant source (i.e., amount loaded to the landscape and groundwater are constant), degradation would require a pattern of decreasing residue concentration with decreasing age date (greater groundwater age), recalcitrance would require stable concentration with decreasing age date. However, loading rates were not constant, but rather would be expected to vary with use on the landscape. For atrazine, Wisconsin use patterns exhibited a rise that began 1960 and leveled in the mid 1970s; for alachlor the rise began about 1970 and leveled in the late 1970s; and for metolachlor the rise began in the late 1970s and leveled within a few years. The case for metolachlor ESA is the most straightforward due to its rapid rise in use. The essentially constant concentration (0.3-0.4 µg L^{-1}; Figures 13 and 14) in 1975-1986 suggests that metolachlor ESA might be stable in groundwater. Though the decline of alachlor ESA over time is consistent with a slow degradation rate, the pattern could also be explained by product of use trends. The atrazine pattern is less clear, and could be used to support arguments that atrazine is stable in groundwater, but again, use trends cloud this conclusion.

26

Table 4. Detected pesticide residues in the till and upper bedrock aquifer.

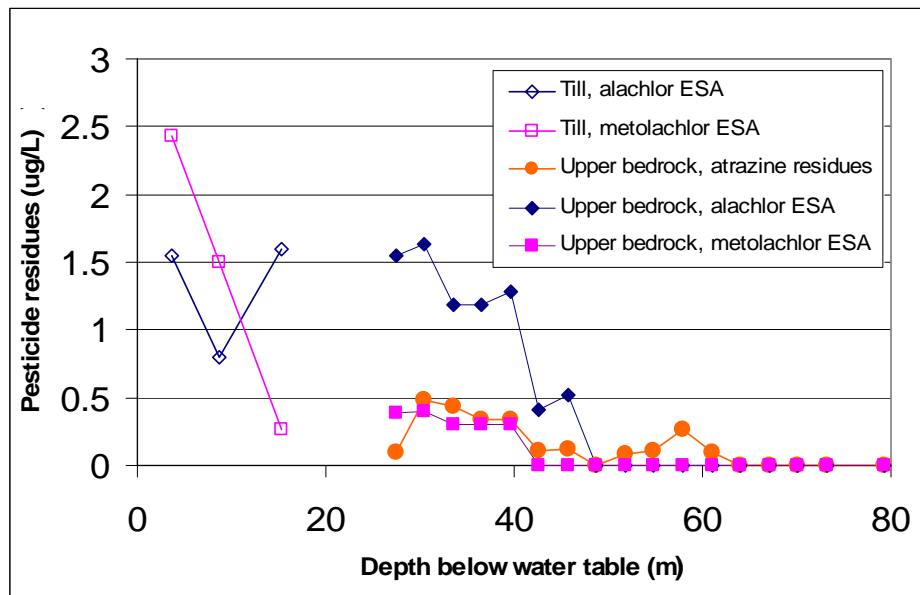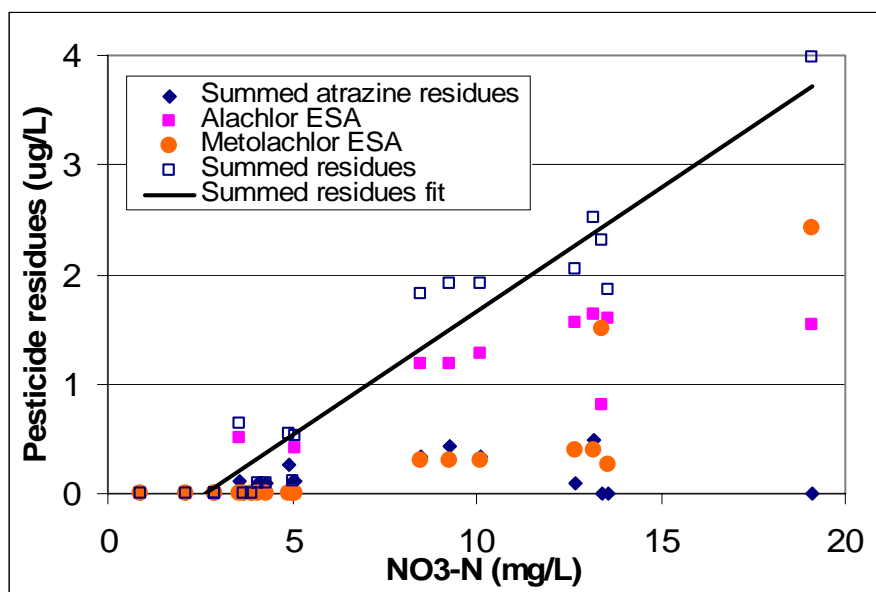| Pesticide residue	Detects (No.)	Detection Limit	Median Detection	Maximum Detection
		---------------- μg L^{-1} ---------------		
Atrazine	10	0.09	0.11	0.16
Deethylatrazine	5	0.2	0.27	0.31
Deisopropylatrazine	1	0.2	0.27	0.27
Total atrazine residues	11	0.1-0.3	0.12	0.48
Alachlor ESA	10	0.4	1.2	1.6
Metolachlor ESA	8	0.12	0.35	2.4
Summed residues	14	0.09-0.4	1.84	4.0

Figure 11. Distribution of pesticides with depth.

Figure 12. Increase in pesticide residue concentration with increasing NO_3-N. Trendline is Total Pesticide Residues = 0.22 NO_3-N - 0.6 (r^2 = 0.93).
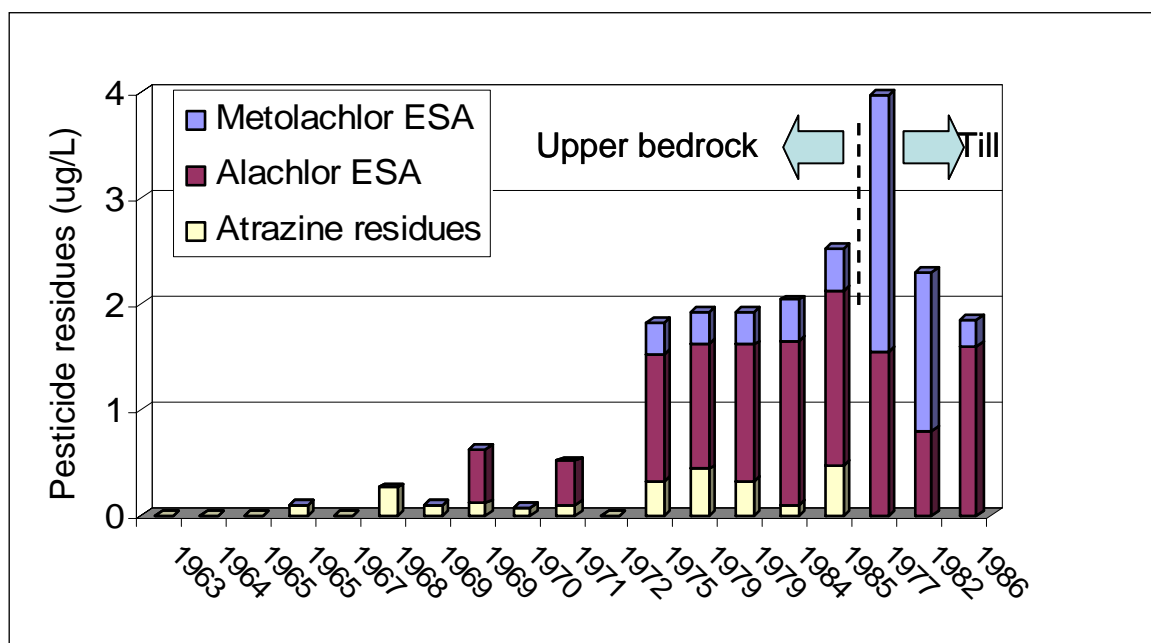

Figure 13. Distribution of pesticide residues with age date.
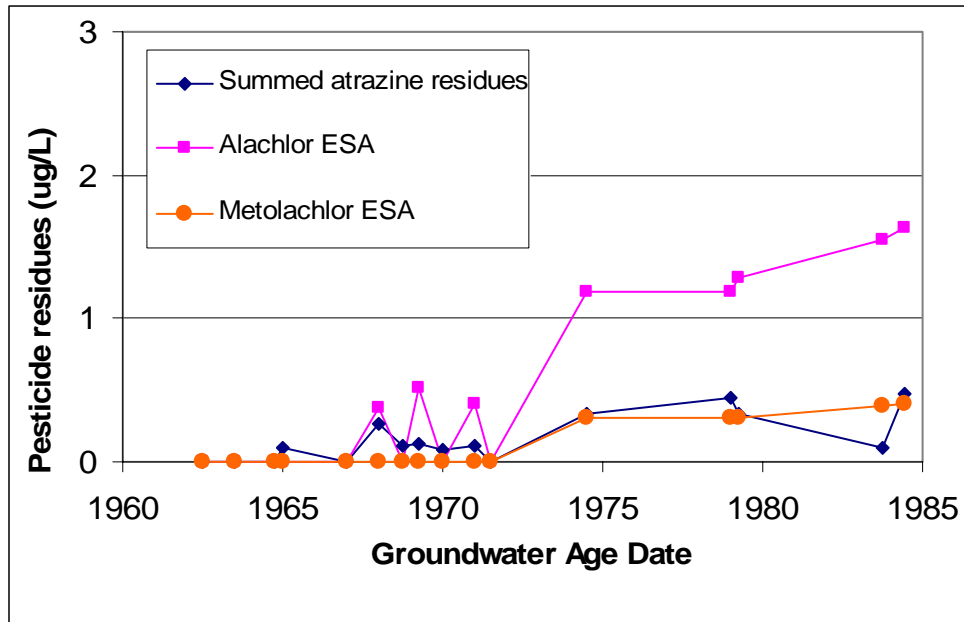
Figure 14. Increase in pesticide residue concentration over time.

DISCUSSION AND CONCLUSION

The profile at Springfield Corners provided access to groundwater flow regimes in the glacial till and the upper bedrock aquifer of northwest Dane County. Till groundwater probably originated from within a few tens of meters of the Springfield Corners site, so its quality was affected by very localized land uses. Till groundwater was of moderately recent origin (1977 to 1986). It contained 13.6 to 19.1 mg L^{-1} of NO_3-N and the pesticide residues metolachlor ESA and alachlor ESA, at summed concentrations ranging up to 4 µg L^{-1}. Denitrification in the till did not remove a substantial portion of NO_3 pollution.

The upper bedrock profile was indicative of larger scale groundwater conditions since groundwater in the profile originated from up to 2-3 km upgradient of the site. Hence, the upper bedrock profile provided a view of conditions generated by the surrounding landscape. Nitrate-N was 13.2 mg L^{-1} at the top of the 57 m thick aquifer, and declined to 0.9 mg L^{-1} at its base. The upper 17 m aquifer exceeded the 10 mg L^{-1} NO_3-N MCL and Wisconsin Groundwater Enforcement Standard. Upper bedrock groundwater exhibited age dates of 1985 (aquifer top) to 1963 (aquifer base). Nitrate increased linearly over time, and crossed a threshold in 1979 whereby incoming recharge began to exceed the NO_3 MCL. Chloride trends paralleled those of NO_3, indicating that the same land management changes that brought about increased N leakage on the landscape also brought about a large increase in Cl. The amount of NO_3-N removed by denitrification in the upper bedrock aquifer was remarkably constant, averaging 2.9 mg L^{-1}. Because of this constancy, denitrification was effective in removing NO_3-N in the more distant past when loads were small compared with later times when loads were great. For instance, denitrification eliminated 73% of the original NO_3 load in the deepest part of the aquifer associated with early 1960s groundwater, but only 16% in shallower part of the aquifer associated with 1980s groundwater. Ultimately, denitrification will not substantially limit NO_3 penetration into the aquifer.

In the upper bedrock aquifer, detected pesticide residues were alachlor ESA, metolachlor ESA, and atrazine with its deethyl-, deisopropyl-, and diamino- degradates. Concentrations of atrazine residues were smaller than much of south central Wisconsin, and those of alachlor ESA and metolachlor ESA were roughly comparable (Vanden Brook et al., 2002; LeMasters and Baldock, 1995). Summed atrazine residues ranged from undetectable (detection limit = 0.09-0.2 µg L^{-1}) to 0.48 µg L^{-1}, substantially below the Wisconsin Enforcement Standard of 3 µg L^{-1}. Alachlor ESA detections were typically 1.0-1.5 µg L^{-1}. Metolachlor ESA concentrations were small (0.3-0.4 µg L^{-1}). Summed pesticide residue concentrations increased with NO_3 and decreased with groundwater age and depth. The earliest age date that an

individual pesticide residue was detected corresponded well to the estimated year of first use of the parent pesticide compound. Evidence strongly supporting degradation of the detected residues in groundwater is lacking, and hence degradation mechanisms may not limit penetration into the aquifer.

Modern pollutant loads do not penetrate the entire upper bedrock aquifer thickness at the Springfield Corners site: denitrification does not limit NO_3 penetration, and groundwater degradation mechanisms may not be limiting pesticide residue penetration (however, residue concentrations are small). Hence, we conclude that an equilibrium does not exist between modern pollutant loading and upper bedrock aquifer groundwater at the study site, and that the aquifer's pollutant load will increase over time. Assuming that under modern practices NO_3-N will increase from the current 5.7 mg L^{-1} profile average to the 13.2 mg L^{-1} displayed in the most recent groundwater (1985), the aquifer average concentration would increase 230% at equilibrium. Because NO_3 trends show no sign of leveling, increases could be greater. The large increase has implications for the aquifer's utility as a drinking water supply, and also for aquatic ecosystem health if export to surface water increases proportionately. Pesticide residue conditions are more difficult to extrapolate into the future. Using an assumption similar to that for NO_3, profile averaged summed pesticide residue concentrations would increase 330%. However, uncertainty about future pesticide use patterns (e.g., current alachlor and atrazine use in Wisconsin is only 3% and 40% of its peak) and degradation rates make attempts to predict future pesticide conditions largely speculative.

The agricultural, hydrological, and geochemical conditions at the Springfield Corners site are similar to much of southcentral and southwest Wisconsin. We conclude therefore that similar increases in groundwater pollutant loads in the Cambrian-Ordovician aquifer could result.

LITERATURE CITED

APHA (American Public Health Association), 1995. Methods for the examination of water and wastewater. American Public Health Association, Washington DC.

Bohlke, J.K. and J.M. Denver. 1995. Combined use of groundwater dating, chemical, and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic coastal plain, Maryland. Wat. Resources Res. 31:2319-2339.

Bradbury, K.R., S.K. Swanson, J.T. Krohelski, and A.K. Fritz. 1999. Hydrogeology of Dane County, Wisconsin. Wisconsin Geological and Natural History Survey Open-File Report 1999-04, 66p.

Browne, B.A. In review 2004. Pumping induced ebullition: A unified and simplified method for measuring multiple dissolved gases. Environ. Sci. Technol. (in review).

Busenberg, E. and L.N. Plummer. 1992. Use of chlorofluorocarbons as hydrologic tracers and age-dating tools: The alluvium and terrace system of central Oklahoma. Water Resour. Res. 28:2257-2283.

Busenberg, E, and L.N. Plummer. 2000. Dating young groundwater with sulfur hexafluoride: natural and anthropogenic sources of sulfur hexafluoride. Water Resources Research 36: 3011-3030.

Clayton, L. and J.W. Attig. 1997. Pleistocene geology of Dane County Wisconsin. Bull. 95. Wisconsin Geological and Natural History Survey. 65 p.

Domenico, P.A. and F.W. Schwartz. 1998. Physical and chemical hydrogeology. John Wiley and Sons, New York. 506 p.

Freeze, R.A. and J.A. Cherry. 1979. Groundwater. Prentice Hall, Inc., Englewood cliffs, N.J.

Glocker, Carl L.   1978. Soil survey of Dane County, Wisconsin. United States Department of Agriculture, Soil Conservation Service in cooperation with the Research Division of the College of Agricultural and Life Sciences, University of Wisconsin.

Heaton, T.H.E. 1981. Dissolved gases: some applications to groundwater research. Trans. Geol. Soc. S. Africa, 84: 91-97.

Kolpin, D.W., M.R. Burkart, and E.M. Thurman. 1993a. Hydrogeologic, water-quality, and land-use data for the reconnaissance of herbicides and nitrate in near-surface aquifers of the midcontinental United States, 1991. U.S. Geol. Surv. Open-File Report 93-418. Washington, D.C.: U.S. Government Printing Office.

Kolpin, D.W., D.A. Goolsby, D.S. Aga, J.L. Iverson, and E.M. Thurman. 1993b. Pesticides in near-surface aquifers: Results of the midcontinental groundwater United States groundwater Reconnaissance, 1991-1992, ed. D.A. Goolsby et al., 64-74. Open File Rep. (U.S. Geol. Surv.) 93-418. Washington, D.C.: U.S. Government Printing Office.

Kolpin, D.W. 1997. Agricultural chemicals in groundwater of the midwestern United States: relations to land use. J. Environ. Qual. 26:1025-1037.

Kolpin, D.W., E.M. Thurman, and D.A. Goolsby. 1996. Occurrence of selected pesticides and their metabolites in near-surface aquifers of the midwestern United States. Environ. Sci. Technol. 30:335-340.

Kraft, G.J. and D.J. Mechenich. 1998. Nitrate and pesticides in domestic water-supply wells for a part of the Town of Stockton, Portage County. Central Wisconsin Groundwater Center. University of Wisconsin - Stevens Point.

Kraft, G.J., B.A. Browne, W.M. DeVita, and D.J. Mechenich. 2004. Nitrate and Pesticide Residue Penetration into a Wisconsin central sand plain Aquifer. College of Natural Resources University of Wisconsin - Stevens Point. 48 pps.

Kraft, G.J. and W. Stites. 2003. Nitrate impacts on groundwater from irrigated-vegetable systems in a humid north-central US sand plain. Agric. Ecosystems Env. 100: 63-74.

Kraft, G.J., W. Stites, and D.J. Mechenich. 1999. Impacts of irrigated vegetable agriculture on a humid north-central U.S. sand plain aquifer. Ground Water 37:572-580.

Krohelski, J.T., K.R. Bradbury, R.J. Hunt, and S.K. Swanson. 2000. Numerical simulation of ground-water flow in Dane County, Wisconsin. Bull. 98. Wisconsin Geological and Natural History Survey. 44p.

LeMasters , G. and J. Baldock, 1995. A survey of atrazine in Wisconsin groundwater. Wisconsin Department of Agriculture Trade and Consumer Protection. ARM Pub 26, Madison, WI

Martin, G.E., D.D. Snow, E. Kim, and R.F. Spalding. 1995. Simultaneous determination of argon and nitrogen. Ground Water 33:781-785.

McMahon, P.B., B.W. Bruce, M.F. Becker, L.M. Pope, and K.F. Dennehy. 2000. Occurrence of Nitrous Oxide in the Central High Plains Aquifer, 1999. Environmental Science and Technology 34:4873-4877.

Meisinger, J.J. and G.W. Randall. 1991. Estimating nitrogen budgets for soil-crop systems. p.85-124. *In* R.F. Follett et al. (ed.) Managing nitrogen for groundwater quality and farm profitability. ASA, CSSA, SSSA, Madison, Wisconsin.

Nehring, R. and A. Grube. 2004. Data compilation from public and proprietary sources. Office of Pesticide Protection. USEPA.

Oberle, S.L. and D.R. Keeney. 1990. Soil type, precipitation, and fertilizer N effects on corn yields. J. Production Agriculture 3:522-527

Puckett, L.J., and Cowdery, T.K., 2002, Transport and fate of nitrate in a glacial outwash aquifer in relation to ground-water age, land use practices and redox processes: Journal of Environmental Quality, vol. 31, no. 3.

Vanden Brook, J., et al., 2002. Agricultural chemicals in Wisconsin groundwater. Wisconsin Department of Agriculture, Trade, and Consumer Protection.

WDNR (Wisconsin Department of Natural Resources. 1996. Groundwater Sampling Field Manual. PUBL-DG-038 96. Wisconsin Department of Natural Resources. Bureau of Drinking Water and Groundwater Madison, Wisconsin: WDNR.

Wentworth, W.E., C. Huamin, and S. Stearns. 1994. Pulsed discharge helium ionization detector - universal detector for inorganic and organic compounds at the low picogram level. J. of Chromatography 688: 135-152.

Zimmerman, L.R., K.A. Hostetler, and E.M. Thurman. 2000. Methods of Analysis by the U.S. Geological Survey Organic Geochemistry Research Group--Determination of Chloroacetanilide Herbicide Metabolites in Water Using High-Performance Liquid Chromatography-Diode Array Detection and High-Performance Liquid Chromatography/Mass Spectrometry. U.S. Geological Survey Open-File Report 00-182

APPENDIX I
MONITORING WELL INFORMATION

Monitoring Well Construction Information

Three monitoring wells were constructed for this study (Table AI-1). Boring logs list the lithology of the unconsolidated till as sandy clay from 0 to 33 m; and silty clayey sand from 33 to 38 m.

Table AI-1. Construction of monitoring wells installed for this study.

Well No.	Well Length (m)	Screen Length (m)	Well material	Nominal Water Depth (m)
SC80	24.4	1.5	50 mm dia PVC	19.9
SC100	30.5	1.5	50 mm dia PVC	20.9
SC125	38.1	1.5	50 mm dia PVC	22.0

APPENDIX II

CORRESPONDENCE OF SAMPLE NUMBERS AND SAMPLED INTERVALS

Table AII-1. Correspondence of sample numbers and sampled intervals.

Sample designation	Depth to interval top (m)	Screen or interval length (m)	Depth below water table (m)	Formation
SC_80	22.9	1.5	3.7	Till
SC_100	29.0	1.5	8.8	Till
SC_125	36.6	1.5	15.3	Till
SC_160	45.7	3.0	27.4	Tunnel City
SC_170	48.8	3.0	30.5	Tunnel City
SC_180	51.8	3.0	33.5	Tunnel City
SC_190	54.9	3.0	36.6	Tunnel City
SC_200	57.9	3.0	39.6	Tunnel City
SC_210	61.0	3.0	42.7	Wonewoc
SC_220	64.0	3.0	45.7	Wonewoc
SC_230	67.1	3.0	48.8	Wonewoc
SC_240	70.1	3.0	51.8	Wonewoc
SC_250	73.2	3.0	54.9	Wonewoc
SC_260	76.2	3.0	57.9	Wonewoc
SC_270	79.2	3.0	61.0	Wonewoc
SC_280	82.3	3.0	64.0	Wonewoc
SC_290	85.3	3.0	67.1	Wonewoc
SC_300	88.4	3.0	70.1	Wonewoc
SC_310	91.4	3.0	73.2	Wonewoc
SC_330	97.5	3.0	79.2	Wonewoc
SC_340	100.6	3.0	82.3	Eau Claire
SC_350	103.6	3.0	85.3	Eau Claire
SC_410	121.9	3.0	103.6	Mt. Simon

APPENDIX III

ANALYTICAL RESULTS

Table III-1. Temperature, pH, specific conductance, DO, and redox potential.

Sample	Temp (^{o}C)	pH	Specific Conductance (uS cm^{-1})	DO (mg L^{-1})
SC_80	11.0	7.67	2073	4.7
SC_100	11.5	7.33	1835	2.47
SC_125	11.6	7.14	937	4.53
SC_160	10.6	7.19	852	7.1
SC_170	10.6	7.22	860	7.1
SC_180	10.4	7.35	786	5
SC_190	10.7	7.36	756	4.6
SC_200	10.5	7.23	787	6.1
SC_210	10.7	7.42	668	3.8
SC_220	10.5	7.33	688	2.4
SC_230	10.5	7.52	644	2.2
SC_240	10.5	7.48	606	5
SC_250	10.4	7.19	573	7.1
SC_260	10.3	7.26	568	6.9
SC_270	10.5	7.41	541	7.1
SC_280	10.5	7.58	519	7.3
SC_290	10.4	7.56	524	7
SC_300	10.6	7.23	458	
SC_310	10.5	7.51	463	5
SC_330	10.4	7.26	486	4.7
SC_340	10.5	7.45	683	6.5
SC_350	10.3	7.34	842	6.5
SC_410	10.3	7.16	848	6.6

Table AIII-2. Major ion concentrations.

Sample ID	Ca	Mg	K	Na	NO3	Cl	SO4	ANC (meas)	ANC (calc)
	- - - - - - - - - - - - - - - - - - mg/L - - - - - - - - - - - - - - - - - -							- - - mmole(-)/L - - -	
SC_80	117.4	67.6	3.5	255.0	19.1	246.0	31.6	8.3	14.4
SC_100	108.0	66.8	3.7	214.0	13.4	385.0	31.8	7.8	8.4
SC_125	77.4	44.9	3.4	123.3	13.6	79.0	31.6	7.9	9.7
SC_160	101.7	53.9	2.5	18.4	12.7	56.5	22.7	7.3	7.9
SC_170	100.2	53.0	2.5	16.9	13.2	49.5	22.9	7.3	7.9
SC_180	91.6	48.4	3.1	14.5	9.3	47.0	18.9	7.0	7.2
SC_190	90.6	47.1	3.3	12.2	8.5	37.5	18.2	6.8	7.3
SC_200	92.2	48.8	2.7	13.2	10.1	42.5	20.1	6.9	7.3
SC_210	80.8	42.7	2.9	8.8	5.1	30.5	15.1	6.6	6.7
SC_220	80.8	42.7	4.0	11.0	3.6	37.0	12.7	6.4	6.7
SC_230	79.9	39.6	4.1	9.1	2.9	30.0	12.4	6.3	6.5
SC_240	71.0	38.6	3.0	7.0	4.1	5.0	15.7	6.1	6.5
SC_250	68.5	37.0	1.5	5.2	5.0	7.1	17.8	5.9	6.1
SC_260	68.6	37.2	1.4	5.1	4.9	6.9	17.7	5.9	6.1
SC_270	65.7	35.5	1.4	4.5	4.3	7.1	17.1	5.6	5.8
SC_280	64.0	33.8	1.3	3.8	3.7	7.3	15.3	5.5	5.6
SC_290	64.8	34.1	1.5	4.7	3.9	8.5	14.6	5.5	5.7
SC_300	63.2	32.7	1.4	4.2	2.9	5.5	11.5	5.3	5.6
SC_310	58.0	30.2	2.1	3.7	2.1	4.0	8.6	5.3	5.2
SC_330	60.9	31.1	2.6	3.8	0.9	3.0	4.1	5.6	5.6
SC_340	78.0	42.3	2.3	11.4	6.7	31.0	14.0	6.4	6.2
SC_350	92.9	50.8	2.7	17.5	11.5	53.0	21.4	7.0	6.8
SC_410	92.5	50.5	2.7	17.4	11.6	54.0	21.3	7.2	6.7

Table AIII-3. Al, Mn, Fe, Si, P, DOC, TKN, and NH_4.

Sample	Al	Mn	Fe	Si	P	DOC	TKN	NH_4
				- - - - mg L-1 - - - -				
SC_80	0.041	0.0250	0.123	9.29	0.035	3.3	0.43	0.04
SC_100	0.989	0.0450	0.148	8.46	0.072	5.7	1.24	0.1
SC_125	0.114	0.0500	0.028	7.83	0.049	2.4	0.99	0.19
SC_160	0.116	0.0005	<0.0006	8.61	0.054	0.7	0.58	0.08
SC_170	<0.006	0.0004	<0.0006	8.67	0.049	0.8	0.123	0.05
SC_180	<0.006	0.0002	<0.0006	8.25	0.08	0.68	0.095	0.073
SC_190	<0.006	0.0003	<0.0006	8.15	0.082	0.6	0.074	0.075
SC_200	<0.006	0.0003	<0.0006	8.27	0.048	0.63	<0.08	0.044
SC_210	0.018	0.0005	<0.0006	7.78	0.034	0.5	0.13	0.03
SC_220	<0.006	0.0004	<0.0006	7.75	0.042	0.8	0.16	0.049
SC_230	<0.006	<0.0001	<0.0006	7.60	0.047	0.54	0.08	0.046
SC_240	<0.006	0.0005	0.013	7.70	0.029	0.44	0.08	0.039
SC_250	<0.006	0.0004	0.0062	7.77	0.019	0.44	0.11	0.023
SC_260	<0.006	0.0004	0.006	7.93	0.017	0.45	<0.08	0.019
SC_270	<0.006	0.0011	0.0545	7.88	0.021	0.42	<0.08	0.033
SC_280	<0.006	0.0009	0.0059	7.84	0.026	0.48	<0.08	0.022
SC_290	<0.006	0.0007	0.0069	7.87	0.019	0.35	0.08	<0.01
SC_300		0.0033	0.0355	7.45	0.016	0.32	0.15	<0.01
SC_310	<0.006	0.0011	0.0101	5.98	0.023	0.35	0.11	<0.01
SC_330	<0.006	0.0014	0.011	5.97	0.018	0.46	0.07	<0.01
SC_340	<0.006	0.0018	0.0169	7.61	0.028	0.58	0.1	<0.01
SC_350	<0.006	0.0024	0.0174	8.63	0.047	0.64	0.04	<0.01
SC_410	<0.006	0.0046	0.0369	8.76	0.044	0.71	0.14	<0.01

Table AIII-4. Pesticide analyses. Undetected pesticide residues not shown.

Sample	Atrazine	Deethylatrazine	Deisopropylatratine	Diaminoatrazine	Total atrazine residues	Alachlor_ESA	Metolachlor_ESA	Total residues
			- µg L-1- -						
SC_80	<0.1	<0.2	<0.2	<0.3	<0.1	1.5	2.4	4.0
SC_100	<0.1	<0.2	<0.2	<0.3	<0.1	0.8	1.5	2.3
SC_125	<0.1	<0.2	<0.2	<0.3	<0.1	1.6	0.3	1.9
SC_160	0.1	<0.2	<0.2	<0.3	0.1	1.6	0.4	2.0
SC_170	0.2	0.3	<0.2	<0.3	0.5	1.6	0.4	2.5
SC_180	0.1	0.3	<0.2	<0.3	0.4	1.2	0.3	1.9
SC_190	0.1	0.2	<0.2	<0.3	0.3	1.2	0.3	1.8
SC_200	0.1	0.2	<0.2	<0.3	0.3	1.3	0.3	1.9
SC_210	0.1	<0.2	<0.2	<0.3	0.1	0.4	<0.12	0.5
SC_220	0.1	<0.2	<0.2	<0.3	0.1	0.5	<0.12	0.6
SC_230	<0.1	<0.2	<0.2	<0.3	<0.1	<.4	<0.12	<0.09
SC_240	0.1	<0.2	<0.2	<0.3	0.1	<.4	<0.12	0.1
SC_250	0.1	<0.2	<0.2	<0.3	0.1	<.4	<0.12	0.1
SC_260	<0.1	<0.2	0.3	<0.3	0.3	<.4	<0.12	0.7
SC_270	0.1	<0.2	<0.2	<0.3	0.1	<.4	<0.12	0.1
SC_280	<0.1	<0.2	<0.2	<0.3	<0.1	<.4	<0.12	<0.09
SC_290	<0.1	<0.2	<0.2	<0.3	<0.1	<.4	<0.12	<0.09
SC_300	<0.1	<0.2	<0.2	<0.3	<0.1	<.4	<0.12	<0.09
SC_310	<0.1	<0.2	<0.2	<0.3	<0.1	<.4	<0.12	<0.09
SC_330	<0.1	<0.2	<0.2	<0.3	<0.1	<.4	<0.12	<0.09
SC_340	0.1	<0.2	<0.2	<0.3	0.1	1.0	0.2	1.3
SC_350	0.1	<0.2	<0.2	<0.3	0.1	1.6	0.3	2.0
SC_410	0.1	<0.2	<0.2	<0.3	0.1	1.6	0.4	2.1

APPENDIX IV

CFC and SF6 Atmospheric Mixing Ratio Histories

(http://water.usgs.gov/lab/cfc/background/Chapter.html#history)

NOAA Air Curves